CHM328S: Modern Physical Chemistry

PROBLEM SET 1

Notes:

- Please start each problem on a new page.
- This problem set is due on Tuesday, February 3, 2009.

1. The mean *speed* v of a particle of mass m at temperature T is

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}},$$

where k is Boltzmann's constant. Show that the root mean square deviation from this average value, defined as

$$\sigma_v = \sqrt{\langle (v - \langle v \rangle)^2 \rangle},$$

is equal to the quantity $\sqrt{\langle v^2 \rangle - \langle v \rangle^2}$. Compute its value and comment on how it depends on m and T. Show that, in general, $\langle v^{2p} \rangle \geq \langle v^p \rangle^2$ for any position integer p.

2. For a particle of mass m at temperature T, calculate the value of $\langle v^4 \rangle$. Assuming that the total energy ϵ of the particle is kinetic energy, so that $\epsilon = mv^2/2$, show that the mean energy per particle is

$$\langle \epsilon \rangle = \frac{3kT}{2},$$

and compute the root mean square deviation $\sqrt{\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2}$. What do you think this measures? Comment on the temperature dependence of this quantity.

3. Consider a collection of N ideal gas particles of radius $R = 1 \cdot 10^{-10}$ m and mass $m = 3.4 \cdot 10^{-27}$ Kg moving in a *three-dimensional* cube of length L at a temperature of $T = 298$ K.

   (a) (10 points) Write down the probability density for the *energy per particle*. What is the most-probable value of the energy per particle?

   (b) Evaluate the fraction of particles with energy $\epsilon \geq 2kT$.